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AUTHORITY

DSTL, WO 189/3094, 8 Oct 2009; DSTL, WO 189/3094, 8 Oct 2009





A REVIEW OF THE LITERATURE ON THE APPLICATIONS OF CW AGENTS WITH RECOMMENDATIONS OF FURTHER RESEARCH ON THICKENED GD [S]

by

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Technical Note No. 256



December 1975

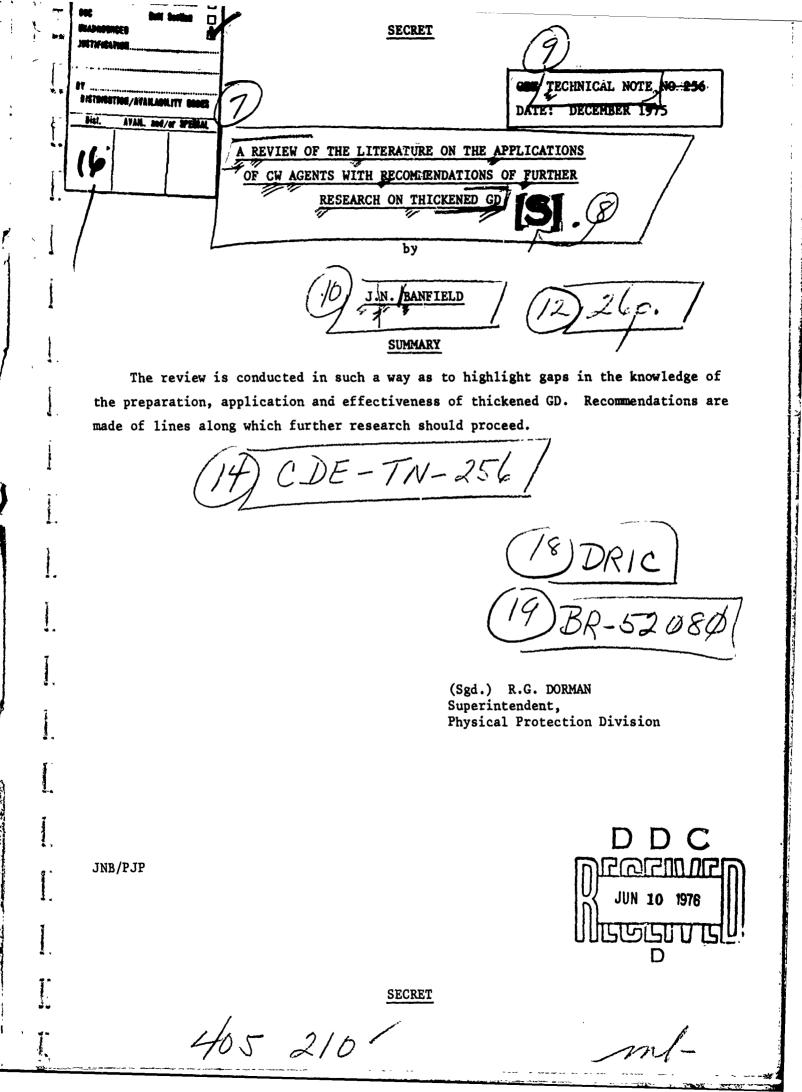
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CDE TECHNICAL NOTE NO 256

DATE: DECEMBER 1975

A REVIEW OF THE LITERATURE ON THE APPLICATIONS

OF CW AGENTS WITH RECOMMENDATIONS OF FURTHER

RESEARCH ON THICKENED GD

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J.N. BANFIELD

INTRODUCTION

- 1. The countries of the Soviet Bloc are known to have stocks of CW Weapons of various types containing thickened GD (1), and there is accordingly a need for the provision of measures of defence against these. However, before effective action in defence research in the strict sense of the expression can be undertaken, it will be necessary to investigate the mode of action of the Soviet weapons. In the absence both of an adequate number of specimens of the weapons and of detailed explanatory literature such an investigation will have to be conducted ab initio; in other words research into weapon design and weapon performance will have to be carried out in the UK. Since the use of thickened chargings has been studied extensively in the UK, the US, and Canada during the last 40 years, the first stage of any new programme of research must be a review of the literature treating of all this past work. It is the purpose of the present Technical Note to carry out such a review and at the same time to offer suggestions as to the most profitable lines of new studies.
- 2. In the interest of clarity it is desirable that the subject of thickened GD be considered under a number of sub-headings; in the present review these will be:
 - (a) the preparation and properties of the thickened agent;
 - (b) its stability in storage and in dispersion;
 - (c) its dispersibility;
 - (d) its persistence in the dispersed state and its availability for "pick-up", ie for transfer from inanimate objects to personnel;
 - (e) its toxicity to personnel both by inhalation of the vapour or of aerosol and by the penetration of the clothing by the liquid or the vapour and the

subsequent penetration of the skin; and

(f) its detection when deposited on the ground and on other inanimate surfaces and the decontamination of those surfaces.

The body of the review will be organized accordingly.

PREPARATION AND PROPERTIES

- 3. The oldest document consulted on the subject of the preparation of thickened CW agents is an unsigned and incomplete Ministry of Supply Monograph (2), which bears no date, but which is indexed as originating in 1945. It deals with the preparation of viscous and viscoelastic forms of "mustard gas" by admixture with natural rubber, chlorinated rubber, polyvinyl acetate (PVA, "gelva") and polymethyl methacrylate (PMMA, "perspex"). After the appearance of this monograph interest in the subject seems to have lapsed for about 20 years, and the next references are to work dating from 1965. Hunt (3) states that the bulk thickening of VX is possible with the addition of PVA or poly-isobutyl methacrylate (PIBM), but that these substances dissolve only slowly in the agent. Russell and Pattle (4) describe the preparation of VX gels with polyvinyl chloride (PVC) alone (4.5%) and with PVC (5.5%) combined with silica flour ("Aerosil 2491") (5.0%), and triethanol-amine stearate (1.0%), and point out that the latter mixture is much more viscous than the former but less thixotropic.
- The preparation of thickened GD is treated by Pattle (5), who recounts the stirring of 5% of PVC into GD at room temperature and the heating of the mixture to 90°C to induce the formation of a gel. Subsequently it was found that the minimum content of PVC required for the establishment of a gel is 4.5% (6). Other thickeners for GD are mentioned by Smith (7), Wills (8) and Bailey (9). Smith gives Versamid 360, a polyamide resin of molecular weight about 7000, and Gelkyd 350, a polyamide-modified polyester resin; the latter is said to be effective not only in GD but also in VX, although as much as 30% is needed to form a gel. Wills cites the polymethacrylates: the methyl and ethyl are insoluble in GD, the butyl and higher ones do dissolve with gel formation. Bailey dissolved PMMA in GD with difficulty but prepared a gel suitable for experiments in decontamination. (It has been discovered recently (10) that PMMA dissolves quite easily in GD, provided it is in the right physical form). In the USA Grula et al (11) have thickened VX, GD, EA 1356, and GB with water-soluble additives, viz forms of hydroxy-propyl cellulose, known commercially as Klucel G, Klucel M, and Klucel HA. By means of these they have obtained solutions in VX having virtually any viscosity desired up to a maximum of 100 poise, and solutions in GD of viscosities as great as 200

poise; with Klucel HA they have prepared a GD gel. The interesting feature of these mixtures is their low content of thickener - nowhere greater than 2%.

5. The theory of the solution of macromolecular substances and the formation of gels is treated in the Monograph mentioned earlier (2), and was also the subject of a recent research contract placed with the University of Wales Institute of Science and Technology (12). The results of the latter appear to indicate that in a gel the polymer chains attract one another at some points, so as to form crystallites, and not at others, but that a great deal more needs to be known for a true understanding of the gelling process. Pattle and Smith (13) announce; in 1966 that they were studying the diffusion of liquids through gels and quoted the formula

$$D_{V} = D_{*} \beta \frac{d \ln a_{A}}{d \ln W_{A}},$$

in which D is the "mutual" diffusion coefficient of the solute and the solvent, D_{\star} is the "tracer" diffusion coefficient of the solvent, and a_{A} and W_{A} are the activity and the volume fraction of the solvent in the gel. Elsewhere they discuss the results of experiments with mixtures of benzene and rubber (14).

6. Although viscous forms of GD and gels have been prepared, it remains to be ascertained that these can be satisfactorily dispersed by spray devices, high explosive etc, and that they are stable in storage. The recommendation of this review is that effort should be held in readiness for the extension of the search for thickening agents, but that the search should not actually be extended, unless it is shown by experiment - preferably on a full scale - that GD thickened or gelled by currently known agents is unsuitable for dispersion or is unstable. In the meantime, since existing knowledge of the physics chemistry and rheology of solutions of polymeric substances is insufficient to permit the systematic consideration of gels and viscoelastic liquids in a CW context, the physical studies mentioned in para 5 must be reviewed with high priority.

STABILITY

7. On the subject of the stability of GD in storage Jackson (15) records that a mixture of 90% GD with 10% VX - unthickened - is stable in an aluminium but not in a steel container. The same worker (16) records that GD thickened with 5.5% PVC and containing 3.24% of di-isopropyl carbodiimide as stabilizer breaks down in a steel container at 71°C after 4 months into a mass of PVC and a separate layer of GD. This separated layer was reported by Bevan (17) to be of good quality.

- 8. Since the stability of GD has clearly not been studied extensively, mention is made here of reports on studies of the stability of other nerve agents, as a forewarning of the amount of effort that may be required for any future work with GD.
- 9. A study of the mechanism of the decomposition in storage of GB was carried out by Marsh and Thomas (18). Similarly oriented studies of the decomposition of V-agents were carried out by Wardrop et al (19,20), who considered both the degradative influence of impurities and the inherent instability of even the pure agents, and by Coult et al (21,22), who were interested in the effect on the agents of gaseous oxygen and the catalysis of that effect by metals. Observations of the storage life of V-agents and the effect thereon of elevated temperature were made by Heggie et al (23), and by Johnson and Koblin (24), the latter being interested additionally in the relative merits of steel and of aluminium containers. Bevan and Maclean (25) investigated the influence on the storage life of VM and VX of a stabilizing additive.

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- 10. Views on the stability of a thickened agent, VX, are expressed by Pattle & Smith (13), Hunt (3), and Jackson (15). When the agent contains only PVC (apart from stabilizer), the mixture appears to be adequately stable (Pattle & Smith). When it contains in addition silica powder and tri-ethanolamine stearate (see para 4), the mixture is <u>less</u> stable than the unthickened agent, the reason being that the silica cannot be freed entirely from adsorbed water (Jackson). Hunt reports that VX thickened with PIBM may be stabilized by the addition of dicyclohezyl carbodimide.
- 11. The little work that has been done on the storage stability of thickened GD appears to indicate that PVC and PIBM are satisfactory additives from this point of view; extensive confirmatory experiments are nevertheless clearly desirable: studies are needed on GD containing other thickeners, in particular those mentioned in para 4, viz Versamid 360, Gelkyd 350, the higher methacrylates and the Klucels. The last named seem to merit some preferential consideration in view of their effectiveness in exceptionally small quantities. It must be recognized however that, since the UK has no commitment to produce CW weapons, the question of stability in storage is not at present one of great practical importance; it is recommended therefore that in the immediate future studies of store life be limited to confirmation that any formulation is sufficiently stable to survive the period of the experimental work planned with it.
- 12. On the subject of the stability of nerve agents in dispersion two reports have been found. The first (26) deals with field trials in which 105 mm shell charged with VX were fired statically and the amount of the agent that survived the explosion was determined by integrations of the ground contamination density and of the total dosage. The extent of the destruction of the agent was about 15%. The second report (27)

treats of the subject of "flashing", ie the ignition of the cloud of vapour or droplets emitted from an exploding device by the hot explosion products or by the shock wave. VX is much more vulnerable to destruction by this means than GB, but the danger of destruction may be appreciably reduced by admixture of the HE charge (Comp B, RDX/TNT) with 15% of oxamide. If GD is to be dispersed explosively - whether in the thickened state or not - similar studies will be required with that agent.

13. The effect of atmospheric moisture on a nerve agent is important, when the agent has been vaporized or dispersed into a spray. This matter is discussed in some depth by Trevaskis (28), who reports that the addition of 10% of mono (or di-) nonylamine to a G or a V agent should ensure that atmospheric moisture does not cause appreciable decomposition in a droplet, before it has evaporated. Trevaskis does not consider vapour phase reactions, nor does he mention GD in any context; the state of knowledge as reviewed by him must therefore be regarded from the point of view of the present Note as doubly incomplete. Studies are clearly required of the stability of GD in the atmosphere both in the form of droplets and in the form of vapour, but it will probably be found preferable to combine these with studies of dispersibility (see below: paras 15 and 19).

DISPERSIBILITY

- The use of a thickener in a nerve agent was proposed primarily to increase its 14. persistence in the dispersed form (4,6), ie to reduce the rate of loss of material from a droplet by evaporation, and to inhibit the tendency of the liquid to seep into the pores of any inanimate body upon the surface of which it may descend and, in so doing, remove itself from a position at which it presents a contact hazard. But this was not the original purpose of thickeners: before the advent of the nerve gases thickeners were admixed with mustard gas etc (2) to control the size of the droplets produced by any shattering process, and especially to ensure that the spray droplets from an aircraft spray tank would be sufficiently large to fall to the ground without being blown far off course by the wind and without "disappearing" into the vapour phase on the way down (29). A thickener must obviously influence dispersion, even when used in a nerve agent, and it is for this reason that the present section of the review has been included. Consideration is given to two processes of dispersion that are of practical interest, namely the aerodynamic break-up of a jet of liquid expelled from an airborne tank, and the explosive dispersion of liquid contained within an artillery shell, an aircraft bomb or a rocket warhead etc.
- 15. A reference to the spraying of GD from a tank has not been found, but work has been done with GB. Milly and Thayer (30) report measurements of vapour dosages over ground sprayed from an aircraft with the unthickened agent from pairs of tanks at

low altitude (25-250 ft) at speeds in the range 220-540 mi/h. They consider that the dosages were not satisfactorily high and suggest that a better result might have been achieved, if the agent had been thickened - ie made more viscous. Other work with GB is reported from Dugway Proving Ground (31) and by Marzulli et al (32). If GD is to be dispersed in this way, it will not be reasonable to assume ab initio that it must be thickened. Since GD evaporates in any given circumstances at only about 1/5 the rate of GB, one must entertain the possibility that the sprayed liquid will survive the process of evaporation sufficiently well to reach the ground in adequate quantities even in the absence of a thickener. Accordingly it is recommended that trials take place in the first instance with unthickened GD, and, if this is not satisfactory, that these trials be followed by trials with viscous mixtures, the viscosity being varied until the desired result is obtained.

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- 16. A great deal of research on aircraft spray techniques has been done by means of simulants, ie non-toxic liquids, whose shattering properties are supposed to be equal to those of one or other of the CW agents of interest. Fish reports the discharge of spray against functional groups of personnel (33,34); Collins (35) reports a study of the effect of aircraft speed on droplet size distribution. Both of these workers were interested in the spraying of "persistent" liquids, ie VX etc; the properties of their simulants cannot therefore be assumed to approximate those of GD, thickened or unthickened. It is accordingly recommended that simulants be developed for every formulation of GD that is to be used in the form of aircraft spray. Since it is virtually impossible to find a second liquid, whose physical properties are all equal to the corresponding ones of a first liquid, it may well be necessary to develop several simulants for each formulation.
- 17. The subject of the dispersion of nerve agents by explosive devices with the measurement of the resulting vapour dosages has occupied several workers: Milly et al report trials with GB in the 5 in AC Rocket (36) and in the 125 lb Chemical Bomb (37); Hadow reports trials with GE in the 25 pr Shell (38); papers from Suffield deal with the dispersion of GB from the 25 pr (39) and the 155 mm Shell (40); two from Dugway Proving Ground deal with that of GA in the 4.5 in Rocket (41) and that of GB in the 105 mm Shell (42); and Hill and Titt consider the use of GB in mortar bombs (43) and in cluster bomblets (44). More work with cluster bomblets has been reported by Floyd (45), describing the attack on a built-up area with GB vapour.
- 18. The use of explosive dispersion with the object of creating contamination by nerve agents in <u>liquid</u> form has received some attention. The dispersion of VX from artillery shell is treated by Dewey and Fish (46) (25 pr), Shaw (47) (155 mm),

Shaw and Peverley (48) (8 in.), and Kerr (49) (105 mm). That of GB has been studied at Dugway Proving Ground (50) (155 mm), at Deseret Test Center (51) (M55 Rocket, M121 155 mm Shell, M23 Landmine), and by two British workers, Wright (52) and Stainer (53). It is interesting to note that, whereas at Dugway appreciable liquid contamination of the ground was achieved, the British workers discount the value of liquid contamination: Wright found little; Stainer observed liquid contamination only in the region in which total lethality would have been achieved by the fragmentation of the shell alone.

19. The explosive dispersion of GD seems to have been considered only at Suffield. In the first of two reports Monaghan (51) describes the bursting of a 155 mm shell but shows that the results were inconclusive. In the second (58) he discusses further trials with the same weapon-agent systems and gives some positive information, but this is very incomplete. There is clearly a need for a thorough investigation of the value of GD as a charging for explosive devices, and it is recommended that a systematic study be undertaken with measurement both of vapour dosages and of liquid contamination densities. For the reasons given in para 14 it is recommended that the study begin with unthickened agent.

PERSISTENCE AND PICK-UP

- 20. Apart from two reports, containing vast quantities of data from trials, which are impossible to evaluate here (56,57), the only reference that has been found to the persistence of GD is that by Russell and Pattle (6). These workers placed drops of GD, both unthickened and thickened (or gelled) by each of several different additives, on isolated leaves of cocksfoot grass in the laboratory, recorded the emission of vapour over a period, wiped off the agent remaining as liquid or gel with a piece of combat sateen, and extracted the agent that had penetrated to the interior of the leaves. They found that the pick-up hazard from GD gelled with 4.5% of PVC is twice that from unthickened GD, and they observed that the reason is that the rate of loss of agent from the contaminated surface by evaporation is reduced as a result of the reduction in the extent of spreading. The fact that the reduction in the rate of evaporation is due to a reduction of spreading and not to a lowering of the vapour pressure was later confirmed by Letts and Plackett (58), whose conclusions are in accord with those of Macy and Zeffert (59) working many years previously with CB.
- 21. As Russell and Pattle imply, there is a need for similar experiments on vegetation other than cocksfoot grass, and the results both of these experiments and of the work they have done already need to be verified by field trials with the "pick-up roller" (60). The persistence of GD on surfaces other than those of leaves also requires attention. It is recommended therefore:

- a. that the laboratory work of Russell and Pattle be extended to all surfaces of practical interest with GD thickened to viscosities throughout the range of practical interest,
- b. that field trials be undertaken with the pick-up roller on grassland and on bare soil of various types,
- c. that suitable non-toxic simulants be developed for each practically useful form of thickened GD for use in experiments on the pick-up of contamination by personnel engaged in defined military functions, and
- d. that such experiments with personnel should be designed to cover the same range of activities as those conducted in the past with simulants of agents other than GD.
- 22. Early studies of the persistence of nerve agents were based only on measurements of vapour dosage and on observations of the time taken for the development of certain fractions of the total. Field trials with neat GB dispersed explosively were carried out at Porton (61), Suffield (62) and Dugway (63,64). The vapour emission from thickened GB was investigated by Koblin and Herd (65), who were interested in the development for the purposes of harassment of a means of creating a concentration in the atmosphere not especially high but lasting for a long time. The evaporation of unthickened VX from the soil and from metal surfaces was measured by Fish and Lyon (66).

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23. Persistence, as manifested by the availability of agent deposited on a surface for pick-up by the clothing of persons making contact with the surface, was first studied - in the field of nerve agents - in connection with the relatively involatile VX. Experiments in the laboratory in which contaminated surfaces of earth, sand, concrete, wood and painted wood were wiped with absorbent pads were conducted by Hassett and Tees (67), whose principal finding was that the degree of transfer of agent to the pads is markedly dependent on the presence of moisture, being slight in very dry conditions. The effect on the pick-up of VX of thickeners was considered by Pattle (68), who used pieces of combat sateen to wipe the surfaces of glass, concrete, brickwork and grass leaves contaminated with VX/PVC and VX/PVC/Silica, and who demonstrated that the thickeners significantly lengthened the period during which VX can be picked up. Field experiments with the pick-up roller were conducted by Reich (69), who worked with neat VX, by Koblin et al (70), who worked with VX made viscous with PIBM, polystytene, PIBM with silica powder and PIBM with chopped sponge, by Banfield and Lewis (71), who worked with VX gelled with PVC, and by Monaghan (72), who used 1/8 in. cubes of sponge in VX thickened very slightly. Banfield and Lewis

measured the pick-up of VX and VM on the trousers of a man sitting on contaminated ground by using a heated dummy wearing clothing (73).

- 24. The transfer of picked-up contamination from the clothing to the skin has been investigated by Brigden (74): working with human volunteers and using a radioactive tracer technique, he measured the transfer of VX labelled with P₃₂ to a finger rubbed across contaminated cloth.
- 25. The pick-up of VX etc by men performing military functions in a contaminated environment has been studied by field experiments with simulants (see para 15). Titt (75) and Reich (76) caused men to crawl individually over ground sprayed with diethyl phthalate from a hand sprayer and then determined the amount of this substance transferred to their clothing. The pick-up of VX simulant by groups of men was studied by Titt (77), Fish (78), Banfield (79) and Stainer and Banfield (8C), the military activities considered including advancing on foot, digging in, defending a dug-in position etc. Finally mention must be made of an experiment of Lewis (81), who compared the pick-up of gelled VX simulant (tributyl phosphate 84%, PVC 9.5%, triethanolamine stearate 1% and Uvitex SWN 0.5%) by the roller with that by a crawling man, and found that, when traversing aged spray, the roller does not accurately simulate the man.
- 26. Since the physical properties of thickened or gelled GD are unlikely to be at all approximate to those of thickened or gelled VX, it is not to be expected that the conclusions of any of the above mentioned experiments will be applicable to GD.

TOXIC EFFECTIVENESS

- 27. Besides being picked up on the clothing from contaminated surfaces, CW agents may attack a man by being inhaled in the form of vapour or aerosol, or by being deposited directly on the clothing or on the skin in the form of droplets or of massive liquid, or by the diffusion of vapour in a contaminated atmosphere into the skin. The subject of toxic effectiveness accordingly embraces the physics of the penetration of clothing fabrics and the biophysics of inhalation and of transfer through the skin, in addition to the physiology of the interference of the agents with vital processes.
- 28. The inhalation toxicity of GD is expressed by Titt (82) and by Hogg (83) in terms of a dosage having a probability of 50% of causing death ie an "LCT50" of 55 mg min/m³. The percutaneous toxicity of unthickened GD is given by Callaway (84) on the basis of experiments with rabbits as a dose having a probability of 50% of causing death ie an "LD50" of 1.46 mg/kg. In respect of GD gelled with 5% PVC the same authority gives differing values, according as the agent is smeared

on the skin or not smeared: they are respectively 1.68 mg/kg and 2.20 mg/kg. Data are also given on the through-clothing percutaneous toxicity of the gelled agent: namely an LD50 of 8.5 mg/kg, if the agent is smeared, and 16.8 mg/kg, if not smeared. Because of analytical difficulties Callaway quotes these figures with some reservations, and more recently, working with pigs instead of rabbits (95), he has found that the percutaneous toxicity of GD/PVC is not greater than that of the unthickened agent.

- 29. The percutaneous toxicity of GD vapour has been investigated by Koon et al (86). These workers exposed clipped, clothed rabbits, breathing clean air, to contaminated armospheres in a range of temperatures, $2 oup 24^{\circ}$ C and found that the LCT50, which does vary significantly with temperature, is approximately 3000 mg min/m³.
- 36. Although clearly the subject of the toxicity of GD has received much attention, the following review of work with other nerve agents will reveal that more needs to be done.
- 31. Studies of the movement of nerve agent through skin include that of Ainsworth (84), who, observing the effect of drop size on the toxicity of VX, estimated that the toxicity would be greater, if the agent were deposited in very small drops (2.0 µm), because the area of skin covered by a stated quantity of VX would then be greater. Ainsworth's conclusion, that at larger drop sizes the effect of drop size is negligible, is confirmed by Weimer et al (88). Marzulli and Wiles (89), comparing percutaneous doses with intra-dermal doses giving the same time to death in rabbits, succeeded in measuring the rate of transfer of VX through the skin: from freely spreading drops the agent penetrates at about 2.5 x 10⁻⁵mm³ per mm² pex minute (ie at a velocity of 2.5 x 10⁻⁵mm/min). Tregear and Dir huber (90) in experiments with pig skin both in vivo and resected showed that so long as the contamination is discontinuous, the rate of transfer of VX is proportional to the contamination density, but that, when the skin is completely wetted, the rate of transfer is constant. Tregear (91) made further measurements of the rate of transfer through skin, using a radioactive tracer technique in experiments with human volunteers. Wiles et al (92) showed that VX is less effective on wet skin than on dry.
- 32. Horton et al (93), Wiles (94), and Allenby et al (95) have considered the effect on percutaneous toxicity of additives. Horton et al showed that a 50/50 mixture of GB with hexafluoroglutaric acid, phosgene oxime, or xylene is significantly more toxic than "pure" GB; they concluded that the effect is due to the inhibition of evaporation. Wiles found that the toxicity of GF was enhanced by the addition of 0.5% of PIBM. Allenby et al showed that the rate of transfer of VX through the skin is $2 \rightarrow 5$ times greater in the presence of 5% of either oxyacids,

dimethyl sulphoxide, or 2-ethylhexylamine.

- 33. The diffusion of nerve gas vapour from the atmosphere into the skin has been the subject of studies by Tregear and Dirnhuber (96) and by Krackow and Fuhr (97). The former, working with excised pig skin and GB, GF and alkyl phosphates, were interested in the physical mechanism of the movement of the vapour into and through the skin. The latter, working with GA vapour and Rhesus monkeys and human volunteers, were concerned to evaluate the toxicity of the vapour: the monkeys, breathing clean air, were killed by dosages in the range 5000 \rightarrow 9000 mg min/m³; the human volunteers, whose arms only were exposed to the vapour, showed no toxic symptoms at dosage levels up to 8000 mg min/m³.
- 34. For completeness, mention is made of the work of Murray (98), Buckholz and McPhail (99) and Thomas and Punte (100), although it is relevant to the purposes of the present Note only insofar as estimates of toxicity to man are based on experiments with hairy animals. These workers all demonstrated a relationship between the LD50 of a V agent sprayed on the skin of an animal and the droplet size, but this relationship is a function of that between droplet size and the ease of retention of a droplet by the hair.
- 35. The migration of nerve agents to the skin through the clothing was investigated by Ainsworth and Truckle (101): by means of experiments with depilated rabbits "wearing" service clothing they showed that drops of GB falling on the clothing are more effective than comparable droplets falling on the bare skin. Subsequently Ainsworth explained this phenomenon by reference to the "storing" of liquid within the pores of the cloth (102). When on the other hand the attacking agent is much less volatile than GB, the clothing offers appreciable protection, as is shown by Clipsham and Mayhood (103) and Chenier and McPhail (104), who worked with VX. Brigden et al (105) discovered that VX is decomposed in clothing, and Wiles et al (92) showed that the decomposition is due to interaction with adsorbed water. Further work on the protection afforded by clothing against attack by V agent has been reported by Weimer et al (88), McDermot et al (106), Ladell and Bramwell (107), Letts and Henville (108), and Alexander (109), the last named comparing the protective qualities of Soviet and Chinese military clothing with the British and the American.
- 36. Some research into the penetration of clothing has been conducted with the use of simulants. Pattle and Smith (14) refer to measurements by Ainsworth of the emission of vapour from tri-n-propyl phosphate gelled with PVC and from triethyl phosphate gelled with PMMA. The emission of vapour from a smeared gelled deposit resembles that from an equivalent quantity of unthickened liquid, that has soaked into the cloth and spread. The effect of gelling apart from subsequent smearing -

is to double the evaporation time. Dennis (110) considered the effect of the velocity of impact of a drop of liquid on cloth on the subsequent emission of vapour.

- 37. It is racommended that studies of the penetration of skin and of clothing by GD, thickened and unthickened, be pursued along the lines of the work cited above with other nerve agents, insofar as it is appropriate.
- 38. No review of toxic effectiveness would be complete without reference to therapy and prophylaxis. GD differs from the other nerve agents in that poisoning by it cannot be relieved by oximes or atropine (111); its prophylaxis and therapy have accordingly given rise to a separate programme of research, which appears to have begun about 10 years ago. Berry and Davies (112) then reported that the prophylactic administration of the <u>carbamate</u> physostigmine together with atropine raises the LD50 of GD by 7 + 8 times. Later Gordon and Leadbeater (113) reported the testing of other carbamates, among them pyridostigmine and mobam (08708); these are more effective than physostigmine and have safety ratios (ie ratios of LD50 to maximum sign free dose) greater than 50. Very recently it has been found (114) that prophylaxis with pyridostigmine and the oxime P2S in conjunction with therapy with atropine and P2S will protect Rhesus monkeys against approximately 28 times the LD50. This work must continue.

DETECTION AND DECONTAMINATION

- 39. The term "detection" used with reference to CW agents may denote either of two distinct processes. These are, first, the establishment of the presence in some place of a particular individual agent or of its having been deposited there in the recent past, and, second, the establishment of the presence of one or more members of a class of agents, characterised by some common biochemical property. The first process involves the identification of the agent itself or of some characteristic product of its degradation under the influence of the environment. Work in this field has been reported by Hambrook et al (115, 116) who show that grass contaminated with 0.5 g/m^2 of GD contains recoverable amounts of certain products of the decomposition of the agent, viz pinacolyl hydrogen methylphosphonate and methylphosphonic acid, as much as 40 weeks later. Since the decomposition products are not especially toxic, the practical applicability of this work seems limited; it may be useful politically however to establish that at some time in the past a CW attack has occurred.
- 40. The second type of detection includes that of agent deposited on solid surfaces and that of agent in the form of aerosol or vapour in the atmosphere. McPherson (117), interested in the contamination of grass, has shown that the Canadian "Paper, Chemical Agent Detector, 3 way, liquid" detects the presence of

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VX thereon with adequate sensitivity. No reports have been found of the paper's having been tested on grassland contaminated with GD. Researchers on the detection of GD deposits seem to be preoccupied with the testing of painted metal surfaces; Hartley et al (118) have reported that the British "Detector Paper No 2 Mark 1" responds reliably to GD on such surfaces. Bailey (119) has pointed out in this connection that the British Detector Paper has been proven only in respect of unthickened GD, being capable of responding to droplets as small as 40 µm in diameter of that agent; its behaviour with the thickened material has not been evaluated.

- 41. It is recommended that the performance of existing detection systems with GD both unthickened and thickened on all surfaces capable of being contaminated be thoroughly investigated, and that the development of new systems should be based as necessary on the outcome of that investigation.
- 42. Methods have been developed for the detection of nerve agents in the atmosphere. The M8 Alarm System, which responds to GD, was regarded as satisfactory in 1971 (112). It is now considered to be insufficiently sensitive and a new system, code-named NAIAD, is being developed (120). Stratford (121) reports that the device in its current state meets the requirement to respond to a concentration of vapour or vapour and aerosol of 2.5 mg/m³ of GD within 5 sec and to a concentration of GD vapour alone of 0.005 mg/m^3 within 5 min. He emphasizes however that it is not reliable in respect of aerosol particles of diameter greater than 10 µm, and that therefore no system exists for the detection of aerosols consisting of particles in the size range from 10 µm up to 40 µm, the lower limit of sensitivity of the Detector Paper (see para 40).
- 43. The subject of GD decontamination is receiving a good deal of attention at CDE at present (9) but only in respect of painted metal surfaces. The treatment of such surfaces affected by unthickened GD was the subject of a recent field trial ("Night Hide"), and a similar trial with thickened GD has been planned for the present year (1). Meanwhile laboratory studies are continuing (9). To the decontamination of surfaces other than that of painted metal no recent reference has been found: Ainsworth in 1964 (122) reported that the PDK fuller's earth pad removes thickened H from various flexible surfaces (melipen, polythene, butyl rubber, nylon 6, neoprene, PVC) as well as it removes unthickened H: he did no tests with GD.
- 44. It remains to consider the decontamination of personnel. Hogg, reporting at length on the PDO ("personal decontamination outfit"), showed (123) that its performance is satisfactory in the removal from the skin of H, GF and VX; he argued

that, since fuller's earth can absorb these liquids, it could be expected to absorb other similar ones. Later Marsh reported that the fuller's earth pad (DKP) was equally effective against neat VX and gelled VX (124) and equally effective against neat GD and gelled GD (125). Tees and Roland-Price, quoting Israeli sources (126), described the Soviet IPP Pack, which will protect against 3 times the percutaneous LD50 of GD - a performance that is not very good in comparison with its effectiveness against VX and GB. Very recently Creasey (127) has examined the Soviet RSD kit (RSD = Russian Skin Decontaminator) and has succeeded in saving the lives of rats contaminated with 28 times the LD50 of GD.

45. The work at present in progress on the treatment of contaminated painted metal must clearly continue; it is recommended that in addition attention be given to the removal of GD from other inanimate surfaces. Efforts should be made to improve the effectiveness of existing types of personal decontaminators against GD - thickened and unthickened - and to develop new systems.

REVIEW OF RECOMMENDATIONS

- 46. The recommendations made at one or more places in each of the preceding sections of this Note are reproduced here in brief with back references.
 - a. Effort must be held in readiness for a further search for additives to GD capable of forming viscous solutions or gels, but, unless the existing formulations are found to be unsatisfactory, the search should not be undertaken. In the meantime high priority should be given to a resumption of fundamental research into the physics and physical chemistry of polymer solutions. (para 6)
 - b. Limited studies of the store life of thickened formulations are required in order to ensure that any sample is sufficiently stable to survive the period of experimental work to be carried out with it. (para 11)
 - c. The feasibility of the effective spraying from an aircraft of unthickened GD must be explored, and consideration must be given thereafter, as necessary, to the spraying of thickened preparations. (paras 13 and 15)
 - d. Further attention is needed to the dispersion of GD by high explosive means. (para 19)
 - e. The persistence of GD, thickened in accordance with all existing formulae, on grassland and various other ground surfaces must be determined. Experiments will be required both in the laboratory and in the field (in the latter with the "standard pick-up roller"). (para 21)

- f. Non-toxic mixtures must be developed to simulate thickened GD of every formulation in studies both of aircraft spray-tank performance and of the movement of personnel over contaminated terrain. (paras 16 and 21)
- g. The penetration of the clothing and the skin by GD needs further study. (para 37).
- h. The development of the prophylaxis and therapy of GD must continue. (para 38)
- i. A means of the detection of GD, thickened and unthickened, on all surfaces that are liable to contamination and that are likely to be in contact with personnel is required. (para 41)
- j. The development of GD decontamination procedures must be extended to all surfaces liable to contamination. (para 45)

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